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# An overview of rare-earth recovery by ion-exchange leaching from ion-adsorption clays of various origins

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**ABSTRACT**

Continuous development of advanced technologies has created increasing demand for rare-earth elements (*REE*), with global emphasis on identifying new alternate sources to ensure adequate supply. Ore deposits containing physically adsorbed lanthanides are substantially lower grade than other *REE* deposit types; however, the low mining and processing costs make them economically attractive as sources of *REE*. To evaluate the commercial potential for the recovery of *REE*s from ion-adsorption deposits in a systematic manner, a standardized procedure for *REE* leaching was developed previously. Using this procudure it was found that, regardless of variations in ore origin and *REE* content, all *REE* consistently reached peak extraction levels under ambient conditions with fast kinetics. Various techniques to improve the *REE* extraction through process variations were also investigated: it was found that decreasing the L:S ratio, re-using leachate on fresh ores and counter-current leaching were all capable of increasing *REE* concentrations in the resultant leachate, albeit at the expense of *REE* extraction levels. In addition, the water content trapped in the leached material was found to contain significant amounts of *REE* and residual lixiviant requiring thorough washing of the solid residue.

**Keywords:** rare-earth elements, ion-exchange leaching, ion-adsorption ores, lanthanide extraction, clay minerals.

## Introduction

Rare-earth elements (*REE*) are a collection of sixteen chemical elements, namely scandium, yttrium and fourteen of the fifteen naturally-occurring lanthanides (excluding promethium); the former two are included as they occur with the latter in the same ore deposits and have similar properties (Cotton, 2006). Their unique properties make them essential for the hi-tech industry. They are used in the manufacturing of high strength permanent magnets, lasers, automotive catalytic converters, fibre optics/superconductors and electronic devices (Gupta and Krishnamurthy, 2005). They are grouped depending on the atomic number, into 'light' rare earth elements (*LREE*) – La, Ce, Pr, Nd, and into 'middle and heavy' *HREE* – Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu. Because of the ongoing development of hi-tech and security applications, there is an increasing demand for *REE* in the international markets, with emphasis on identifying new resources to ensure adequate supply for present and future use. In terms of ore reserves and mineral resources, China dominates the world with reserves estimated to be around 50% of the total, followed by Australia, Russia, Canada and Brazil, while completely leading and controlling the global production at ~90% (Weng *et al*., 2015). A review of rare-earth deposits of North America by Castor (2008) concludes that world reserves are sufficient to meet international demand for most *LREE*, but the *HREE* such as dysprosium will become scarce because the current source of *HREE* is limited to ion-adsorption deposits in China. Consequently, ion-adsorption clay deposits in other parts of the world have gained interest as sources of *HREE*. For the last 3 decades, R&D in the field of *REE* in most of the Western world has

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slowed down due to the import of these elements from China. Consequently, the development of specialized extraction, refining and processing technologies, including equipment and training of engineering expertise, were allowed to lapse, thus creating a dependence on Chinese supplies (Hurst, 2010). Starting in 2005, China – the undisputed leader in both *REE* mining and trade, started restricting yearly export quotas for *HREE*, in order to have enough resources for its own industries and to gain control over the global market (Wübbeke, 2013). Consequently, the last decade has brought a renewed concerted global drive towards *REE* research and development, led by the major end-users of rare-earth products, such as the European Union, USA and Japan, with the dual scope of finding new resources and improving processing/extraction technologies, as summarized by Adachi *et al*. (2010). Following negotiations with the World Trade Organization (WTO), China eliminated rare-earth oxides (REO) export restrictions in 2014, causing a fall in the *REE* prices in the international markets (Wang *et al*., 2015).

Rare-earth elements are incorporated in accessory minerals in various rocks, but the most commercially significant sources, as reviewed by Kanazawa and Kamitani (2006) and more recently described in the comprehensive assessment by Weng *et al*. (2015) are presented below:

(1) Bastnäsite, (*REE*)($CO_3$)F, is a fluorocarbonate mineral containing 65–75 wt.% light REO and accounts for more than 80% of global REO production. The two major sources in the world for lanthanides are bastnäsite deposits at Mountain Pass, California (USA, owned by Molycorp Inc. – devoted solely to *REE* production, and Bayan-Obo, Inner Mongolia (China) – mined primarily for iron ore and *REE* as a by-product (also containing monazite). In August 2015, due to a global decline in *REE* prices, the rare-earth production at Mountain Pass was suspended and the facility was moved to 'Care and Maintenance', while Molycorp Inc. filed restructuring plans which included selling the Mountain Pass assets (Molycorp News Releases, 2015*a*,*b*).

(2) Monazite, (*REE*)$PO_4$ is a *LREE* phosphate containing 55–65 wt.% REO, associated with granites and beach sands in Australia, Brazil and India; the Mount Weld deposit in Western Australia, owned by Lynas Corp., contains one of the highest grade *REE* deposits in the world. Until about 1965 monazite was the main *REE* source; since then, the use of monazite has been considerably reduced due to radioactivity caused by thorium and radium.

(3) Xenotime (Y,*REE*)$PO_4$ is an yttrium-rich phosphate containing 25–60 wt.% $Y_2O_3$ and other heavy *REE*. It is recovered mainly as a by-product of mining for titanium, zirconium and tin in Malaysia, Indonesia and Thailand.

(4) Weathered crust elution-deposited rare earth ores (ion-adsorption ores) are aluminosilicate minerals (e.g. kaolinite, illite and smectite) containing 0.05–0.3 wt.% *REEs* physically adsorbed at sites of permanent negative charge (Chi and Tian, 2008). The ion-adsorption clay deposits are the result of *in situ* weathering of host rocks (mainly granitic), which, over geological timescales, results in the formation of aluminosilicate clays. Clay minerals are part of the phyllosilicate class, containing layered structures of shared octahedral aluminium and tetrahedral silicon sheets, allowing water molecules and hydrated cations to move in and out of the interlayer spaces (Velde and Meunier, 2008). Very commonly, isomorphous substitution of one cation with another (of similar size but with lesser charge, e.g. $Al^{3+}$ for $Si^{4+}$ or $Mg^{2+}$ for $Al^{3+}$) within crystal structures leads to a charge imbalance in silicate clays, which accounts for the permanent negative charge on clay particles, and thus the capability of adsorbing lanthanide ions released/dissolved from precursor *REE*-bearing minerals during weathering (Meunier, 2005). Warm tropical and sub-tropical climates present ideal conditions for this process to occur (Sanematsu *et al*., 2013). The best example of this formation process exists in Asia, where many such deposits are known to exist, as described by Bao and Zhao (2008), Murakami and Ishihara (2008) and more recently by Sanematsu *et al*. (2013). Regardless of the low grades, ion-adsorption clays account for ~35% of the China's total *REE* output and ~80% of world's *HREE* production (Yang *et al*., 2013). It is estimated that the production of ion-adsorbed rare earths will increase yearly by ~1.7% and peak in 2024 at 45,793 t (Wang *et al*., 2015).

Carbonate and phosphate sources, of high grade, are associated with elevated recovery costs due to separation, beneficiation and need for aggressive conditions to dissolve the *REE*. For example, bastnäsite is generally leached with concentrated $H_2SO_4$ or HCl, whereas monazite/xenotime concentrates need to be baked either in 98% $H_2SO_4$ or 70% NaOH to render the *REE* soluble (Gupta and Krishnamurthy, 2005). According to Castor (2008) other *REE* deposits in North America in addition to bastnäsite consist of the so-called 'hard-rock' peralkaline ores including zircon, titanate, niobate, allanite, eudialyte, gadolinite; these deposits are enriched in *HREE* but require harsh conditions to break down the mineral matrix (e.g. caustic bake followed by acid leaching); the processing of these ores is directed mainly towards extraction of niobium, tantalum and zirconium (Gupta and Krishnamurthy, 2005).

The route followed by the European Union to improve resource efficiency is via creation of alternative sources through innovations in the field of reuse and recycle of rare-earth wastes such as magnets and polishing powders (ERECON, 2015). Although recycling from priority streams such as fluorescent light bulbs and batteries is presently feasible, and potential *REE*-rich sources reaching end-of-life, such as hard disk drives, wind turbines, magnets and automotive catalytic converters can be considered for the near-future processing sources, recycling rates at present are still very low (<1%) and there are no large scale commercially viable *REE* recycling operations (Massari and Ruberti, 2013).

Ion-adsorption type deposits are substantially lower grade than other types of lanthanide sources (Kanazawa and Kamitani, 2006), nominally requiring higher costs for *REE* extraction and recovery. However, this disadvantage is largely offset by the easier mining and processing costs, and the relatively low content of radioactive elements such as thorium and uranium (Murakami and Ishihara, 2008). These deposits are mined by open-pit methods and no ore beneficiation is required. A simple leach using monovalent sulfate or chloride salt solutions at ambient temperature can produce a high-grade REO product, as described by Chi and Tian (2008) and more recently Moldoveanu and Papangelakis (2012, 2013). Because of their abundance in surface layers in nature, ease of mining and processing, these clays warrant a detailed study as important sources of rare earths.

## Formation of weathered crust elution-deposited rare-earth ores (ion-adsorption clays)

The ion adsorption *REE* deposits were first discovered in 1969 in the Jiangxi Province (southern China) and declared a novel type of exogenous rare-earth ore (Chi and Tian, 2008).

The formation of this ore type is due to physical, chemical and biological (microbially-assisted) weathering of *REE*-rich granitic and volcanic rocks under warm, humid, slightly acidic conditions in subtropical zones. According to Bao and Zhao (2008), the weathering crusts are up to 30 m deep and divided into four layers: (A) An upper humic layer of quartz, organic matter and soil: 0–2 m thick, with very low/nil *REE* content; (B) a strongly weathered layer enriched in *REE*: 5–10 m thick with kaolinite, halloysite, quartz and mica; (C) a semi-weathered layer: 3–5 m thick with kaolinite and sericite; (D) a weakly-weathered bottom layer with the same mineral composition as the host rock. Up to 80–90% of the adsorbed *REE* are hosted by the strongly weathered layer (B), whereas <15% are found in the semi-weathered layer (C). Depending on the nature of the original host rocks, the general components of the weathered ores are kaolinite, halloysite and muscovite, with a typical composition (as wt.%) of ~70% $SiO_2$, 15% $Al_2O_3$, 3–5% $K_2O$, 2–3% $Fe_2O_3$ and less than 0.5% of CaO, MgO and other elements (Ishihara *et al*., 2008; Weng *et al*., 2015).

Considering the geological and climate conditions for the formation of *REE*-bearing weathered ores, there is no reason to limit the occurrence of this type of deposit within Chinese borders. While at the present time China is the only country to actively pursue and develop this type of resource to commercially produce *REE*, recent geological surveys (summarized by Weng *et al*., 2015) have led to the discovery and investigation of similar ion-adsorption clay deposits in South America (Rocha *et al*., 2013) and Africa (TRE Project, 2014) located in the same warm sub-tropical and tropical weathering areas.

## Nature of rare-earth elements in ion-adsorption ores

As explained above, the ion-adsorption ores contain clays with permanent negative surface charge, which is responsible for cation (such as *REE*) adsorption via electrostatic bonds (Meunier, 2005).

According to Bradbury and Baeyens (2002) as well as Piasecki and Sverjensky (2008), for acidic and near-neutral conditions ($pH < 6.5–6.8$), most of the surface-adsorbed extractable lanthanides occur as simple or hydrated cations such as 'clay-*REE*' or 'clay-$REE(H_2O)_n$' species derived from straightforward cation-exchange reversible reactions at the permanent negative charge sites on the clays (physisorption); for $pH > 7$ the prevalent forms are the irreversibly-fixed hydrolysed 'clay-O-$REE^{2+}$' species derived from permanent complexation reactions at the amphoteric surface hydroxyl groups (chemisorption) (Chi and Tian, 2008).

Due to various weathering conditions (i.e. nature of host rocks, water and soil pH, temperature, pressure, redox conditions) there are three main categories of *REE* present in the ion-adsorption clays, as described by Chi *et al*. (2005) as follows. (1) Colloid phase: *REE* deposited as insoluble oxides or hydroxides or as part of colloidal polymeric organometallic compounds. These species have low occurrence in ores at the slightly acidic natural conditions and can be recovered only by acid leaching. (2) Exchangeable phase: *REE* occur as soluble free cations/hydrated cations or part of positively-charged complexes in solution adsorbed species on clays. These species account for 60–90% of the total content of rare earths in ores and can be recovered by ion-exchange leaching with monovalent salts. (3) Mineral phase: *REE* are part of solid fine particles with same mineral matrix as the host rocks (*REE* part of the crystal lattice). This phase usually accounts for the balance from the ion-exchangeable phase towards the total rare-earth content (T*REE*) content and can be recovered only by decomposition of mineral phases by alkaline bake or acid leach.

The vast majority of the ion-adsorption ores present a 'negative cerium anomaly', as described by Chi *et al*. (2005), Bao and Zhao (2008) and Sanematsu *et al*. (2013), meaning that there is a relative depletion in the normalized (usually to chondritic concentration) concentration of Ce compared to La and Pr. This is due to the fact that, contrary to the majority of lanthanide elements, which are usually adsorbed physically as trivalent ions, $Ce^{3+}$ can be oxidized easily by atmospheric oxygen ($O_2$) to $Ce^{4+}$ (Bard *et al*., 1985), and precipitate as cerianite, $CeO_2$. Additionally, $Ce^{3+}$ can be oxidized to $Ce^{4+}$ during adsorption on δ-$MnO_2$, as described by Ohta and Kawabe (2001). Consequently, these processes facilitate a natural separation of Ce from the other adsorbed trivalent lanthanides and lead to low recovery of Ce by ion-exchange reactions.

Depending on the nature of the original host rocks, other metals will become dissolved and carried downstream during the weathering, decomposition and alteration processes. The main impurities associated with the ion-adsorption ores are usually Al, Na, K, Mg, Ca, Mn, Zn and Fe. While most base metals occur as part of the mineral matrix and do not leach out during the mild ion-exchange *REE* leaching conditions, a certain fraction of Al (due to its trivalent state) and to a lesser extent Na, K, Ca and Mg are adsorbed physically and become liable to be dissolved during the process along with the lanthanides, as reported by Chi and Tian (2008) and Rocha *et al*. (2013).

## Overview of leaching technologies for the ion-adsorption clays

As described previously, the ion-adsorption clays contain 0.05 to 0.3 wt.% *REE*, of which generally more than 60% occur as physically adsorbed species recoverable by simple ion-exchange leaching (Chi and Tian, 2008; Chi *et al*., 2013, Tian *et al*., 2013; Luo *et al*., 2014). Typically, the ores are leached with concentrated inorganic salt solutions of monovalent cations. During leaching, the physisorbed *REE* are relatively easily and selectively desorbed and substituted on the substrate by the monovalent ions and transferred into solution as soluble sulfates or chlorides, following a theoretical 3:1 stoichiometry (equation 1). However, the actual lixiviant usage generally exceeds the stoichiometric requirements due to competing desorption of other cations (such as Al) also adsorbed on clays. Dissolved *REE* are usually selectively precipitated with oxalic acid to form oxalates (equation 2) that are subsequently converted to REO via roasting at 900°C according to equation 3. Finally, the mixed REO are separated into individual *REE* by dissolution in HCl and fractional solvent extraction.

$$2\ \text{Clay}-REE + 3\text{M}_2\text{SO}_4 \rightarrow 2\ \text{Clay}-\text{M}_3 + REE_2(\text{SO}_4)_3 \quad (1)$$

$$REE_2(\text{SO}_4)_3 + 3\text{H}_2\text{C}_2\text{O}_4 + 10\text{H}_2\text{O} \rightarrow REE_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \quad (2)$$

$$REE_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O} \rightarrow REE_2\text{O}_3 + 3\text{CO} + 3\text{CO}_2 + 10\text{H}_2\text{O} \quad (3)$$

Various investigations of the desorption of *REE* from clays via ion-exchange leaching (Chi and Tian, 2008; Moldoveanu and Papangelakis, 2012, 2013) indicated that, regardless of the initial content, not all *REE* reached similar extraction levels (i.e. the percentages of desorbed/recovered *REE* varied widely). Coppin *et al*. (2002) reported that the amount of trivalent lanthanide ions adsorbed on smectite and kaolinite was inversely proportional to the ionic radii and pointed to a fractionation during selective sorption of lanthanides, with heavy elements (i.e. higher atomic number: Tb to Lu) being adsorbed stronger that the light ones (i.e La to Gd). They related this behaviour to the lanthanide contraction in the ionic radii going from light to heavy *REE*. Based on these observations, it was inferred that desorption must exhibit a similar trend, with *HREE* being more difficult to extract, probably according the trend La > Ce > Pr > Nd > Sm > Eu > Gd > Tb > Dy > Ho > Y > Er > Tm > Yb > Lu.

Ever since the discovery of the weathered crust elution-deposited rare-earth ores, China has employed the ion-exchange leaching procedure for the extraction of lanthanides via three successive generations of technology, as summarized by Chi *et al*. (2013) and presented below.

### *The first-generation leaching technology – batch leaching with NaCl*

In the early 1970s, the ores were processed by opencast mining, sieved and leached with ~1 M NaCl in barrels, followed by oxalic acid precipitation. The main disadvantages of this initial approach were small scale, low yields, high lixiviant concentration needed and poor product quality (<70% total rare-earth oxide content due to Na oxalate coprecipitation), which greatly surpassed the advantages of extremely low costs and fast processing times. By the mid-1970s the procedure was changed to bath leaching in concrete pools in order to increase production; however, the main disadvantage of low product purity remained and, because of the largely unregulated and illegal/clandestine mining and extraction practices, the environmental impact was devastating, including severe loss of vegetation and biodiversity, soil erosion and water contamination (both streams and phreatic).

### *The second-generation leaching technology – batch and heap leaching with $(NH_4)_2SO_4$*

In the early 1980s, 1 M NaCl solution was replaced by ~0.3 M $(NH_4)_2SO_4$ solution as lixiviant for batch leaching, which required less reagent consumption due to increased desorption capabilities of $NH_4^+$ as compared to $Na^+$ and led to improved final product purity (Chi *et al*., 2013). The procedure was so successful that it became the primary leaching method for the next ~20 years and contributed largely to the intense development of *REE* ion-adsorption research. However, the second-generation batch leaching technology led to environmental impact as well, due to mining-related deforestation and discharge of tailings and was ultimately replaced in the early 1990s by the heap leaching procedure (Yang *et al*., 2013).

In the traditional heap leaching procedure, the soil pile (1.5–5 m high) is built on a flat impermeable (leak-proof) layer 5–20 cm thick inside a cofferdam ~50 cm high to prevent solution overflow. The lixiviant is injected into the top of the pile at a solid to liquid (S:L) ratio of ~0.25:1 and accumulates at the bottom in the collecting ditch. Washing is performed with clean water at a S:L ratio of ~0.6:1; depending on the size of the ore heap, leaching time ranges from 100 to 320 h and *REE* extraction can reach up to 90%. This procedure is very well suited for the processing of very low-grade ores.

### *The third-generation leaching technology – in situ leaching with $(NH_4)_2SO_4$*

The intense and largely unregulated use of successful batch and heap leaching with ammonium sulfate for ~2 decades led to severe and long-lasting environmental, ecological and health damages in southern China; as an example based on data presented by Yang *et al*. (2013), by 2010 the *REE* mining in Guangdong Province alone has left ~302 abandoned mines, 191 million tons of tailings and 153 km$^2$ of destroyed forests.

In June 2011, in an effort to regulate the industry and deal with the environmental effects, the Chinese government enforced a ban on surface mining and batch/heap leaching while implementing mandatory *in situ* leaching technology for the processing of the ion-adsorption ores, as being more advantageous in terms of surface vegetation clearing and soil disturbance (Yang *et al*., 2013; Wang *et al*., 2015). The basic principle of *in situ* leaching (also called 'solution mining') is injection of leaching solution directly into the natural orebody and retrieval of the pregnant solutions for further processing. Leaching holes with a depth of 1.5–3 m and diameter of ~0.8 m are drilled 2–3 m apart, for up to 100 m, the lixiviant (~0.3 M $(NH_4)_2SO_4$) is injected at high pressure, flows through the pores of the orebody and the loaded leach solution is pumped above-ground through the recovery wells; depending on the adsorbed *REE* content and degree of weathering the whole process (including injection of water for washing) can take up to 400 days before reaching maximum possible *REE* extraction.

The *in situ* leaching technique is also currently applied in China for the recovery of residual *REE* from very low-grade ores and the tailings of older batch and heap leaching operations (Chi *et al*., 2014).

The implementation of *in situ* leaching requires comprehensive geological surveys – specific to each site – in order to determine the hydrogeological structure of the area, ore characteristics, grade, orientation and the surrounding rock infiltration properties. The procedure can only be applied to an orebody with suitable permeability and placed over solid bedrock without fissures. Failure to conduct diligent geological surveys may result in serious environmental degradation such as underground water contamination, mine collapse, landslides and severe loss of *REE* recovery (Li, 2011; Chi *et al*., 2014).

Recent trends in ion-adsorption ore research are focused on minimizing the consumption of ammonium sulfate for *in situ* leaching, in an effort to reduce ammonia pollution of surface and ground waters, either by adding certain leaching-enhancing additives to the conventional $(NH_4)_2SO_4$ lixiviant or by evaluating alternative leaching reagents, as described below. Small additions (0.03–0.1%) of natural organic reagents such as the plant derivative *Sesbania Gum* (Tian *et al*., 2013) and humic acids (Luo *et al*., 2014) to ammonium sulfate have been proven to increase T*REE* extraction by up to 8% and improve the leaching rate. Although neither group offers a fundamental explanation of the reported phenomena, we believe that it is an increased solubility effect via the formation of soluble *REE*-organic complexes due to the chelation power of the many hydroxyl groups contained in the organic additives.

Xiao *et al.* (2015 *a*) assessed the use of magnesium sulfate for leaching of ion-adsorption clays from southern China, with the dual aim of replacing ammonium-based lixiviants and correcting a magnesium (well-known nutrient) deficiency problem encountered for the soils in that particular region. It was considered that the long-term environmental advantages of using magnesium sulfate far exceeded the losses in production due to the small decrease in *REE* extraction (5–7%) as compared to ammonium sulfate. An additional benefit of using $MgSO_4$ instead of $(NH_4)_2SO_4$ is the 10–15% decrease in aluminium desorption, which translates into a lower solution impurity content to be processed/eliminated downstream (Xiao *et al.*, 2015 *a*).

## Evaluation of leaching potential of various ion-adsorption ores

As new ion-adsorption *REE* deposits are being explored and discovered in the rest of the world, research on *REE* extraction from ores has expanded outside of China as well. For the last six years, the University of Toronto has conducted systematic in-depth studies on the leaching chemistry and optimum conditions for *REE* extraction from clay samples obtained from various geographical locations. Overall, it was determined that, under atmospheric conditions, the leaching efficiency of monovalent ions for *REE* extraction depends on the hydration energy of the exchange ion, following the order $Cs^+ > NH_4^+ > K^+ > Na^+ > Li^+$, in both sulfate and chloride systems (Moldoveanu and Papangelakis, 2012). While $Cs^+$ performed best in terms of leaching power, for economic and environmental reasons $NH_4^+$-based lixiviants would be the more practical choice. Batch leaching studies also revealed that the ion exchange process achieved equilibrium in as little as 5 min, regardless of the experimental conditions; ambient temperatures and moderately acidic pH values (5–5.5) represent optimum conditions for maximum *REE* recovery, as massive lanthanide hydrolysis is expected to occur at pH above 6.8–7, whereas high temperature tends to lower the hydrolysis pH values (Moldoveanu and Papangelakis, 2013).

Based on those previous studies, a benchmark batch leaching procedure was established and research has been conducted at the University of Toronto in order to compare leaching characteristics among different ore samples obtained from Africa (Madagascar), South-East Asia (outside China) and South America (Brazil) (exact location and specifics of deposits subject to confidentiality agreements between authors and the mining companies providing the samples) and evaluate lanthanide extraction. The final aim is to develop a fully contained optimized process for field implementation that minimizes the impact to the environment by providing options for efficient reagent use, maximized extraction and recycling/regeneration of the lixiviant (Cheuk *et al*., 2014).

## Experimental methodology

### *Solid characterization*

The *REE* contents of the ore samples were determined by acid digestion for 30 min at 220°C according to the following procedure: 0.5 g crushed ore samples were added to 15 ml *aqua regia* (a mixture in volumetric ratio of 3:1 of concentrated HCl and $HNO_3$, respectively) and placed in hermetically closed pressurized vials inside the Ethos EZ Microwave Digestion System (Nieuwenhuize and Poley-Vos, 1991). Following digestion, the liquid

TABLE 1. Total *REE* content of ion-adsorption clays from different geographical origins.

| Origin | Africa | | | | | Asia | | S. America |
|---|---|---|---|---|---|---|---|---|
| *REE* (ppm) | A1 | A2 | A3 | A4 | A5 | B1 | B2 | C1 |
| Y | 290 | 140 | 180 | 120 | 100 | 1570 | 470 | 1200 |
| La | 1750 | 290 | 1790 | 460 | 250 | 70 | 980 | 450 |
| Ce | 260 | 170 | 220 | 450 | 280 | 60 | 200 | 120 |
| Pr | 280 | 70 | 270 | 120 | 40 | 30 | 190 | 100 |
| Nd | 1000 | 230 | 880 | 260 | 160 | 120 | 690 | 290 |
| Sm | 170 | 40 | 170 | 60 | 40 | 40 | 180 | 60 |
| Eu | 10 | 10 | 10 | 1.76 | 4.76 | 0.636 | 10 | 20 |
| Gd | 110 | 40 | 90 | 30 | 30 | 150 | 130 | 100 |
| Tb | 20 | 10 | 10 | 10 | 1.06 | 40 | 20 | 60 |
| Dy | 60 | 20 | 20 | 20 | 10 | 260 | 100 | 220 |
| Ho | 10 | 10 | 4.6 | 3.33 | 1.43 | 50 | 20 | 70 |
| Er | 20 | 10 | 150 | 120 | 10 | 380 | 250 | 210 |
| Tm | 2 | 0.869 | 0.685 | 0.0232 | 10 | 40 | 20 | 50 |
| Yb | 20 | 10 | 10 | 10 | 0 | 160 | 30 | 260 |
| Lu | 2.66 | 2.66 | 2.53 | 1.71 | 2.4 | 20 | 4.95 | 50 |
| T*REE* | 3990 | 1080 | 3800 | 1650 | 950 | 3000 | 3300 | 3260 |

samples were filtered, diluted with 5% $HNO_3$ and the *REE* content was determined by inductively coupled plasma optical emission spectrometry (Agilent 720 ICP-OES) of the solution; *REE* standards (Inorganic Ventures) in the range 0–20 ppm were used.

### *Batch leaching tests*

The leach solutions were prepared using ACS reagent grade ammonium sulfate and deionized water. The benchmarked procedure for leaching is: 0.5M $(NH_4)_2SO_4$ (natural pH ~ 5.2), ambient conditions, liquid to solid (L:S) ratio of 2:1 (vol./mass), 30 min total time. The slurry was agitated via magnetic stirring then the mother liquor was separated by vacuum filtration. The filter cake was washed by deionized water of pH 5 (2 × 100 ml), and the wash water was collected separately for analysis. The resultant loaded solutions were diluted with 5% (vol.) nitric acid and analysed by ICP-OES to calculate the *REE* extractions.

### *Column leaching tests*

After being homogenized and pelletized (agglomerated) to a size of ~2 μm, ~220 g of ore sample (bed height 300 mm) was placed in a glass leaching column with an inner diameter of 30 mm; a fibreglass filter plate was fixed at the bottom of the leaching column to retain soil particles and one was placed on top of the ore sample to resist preferential flow (even liquid dispersion). The lixiviant (0.5 M $(NH_4)_2SO_4$ solution) was added into the leaching column via a peristaltic pump at a constant flow rate of 0.4 ml/min. The sampling was done every 10 ml for 48 h and the loaded solution was diluted with 5% $HNO_3$ and stored for further analysis; afterwards, the column was flushed with deionized water of pH 5 for 33 h (at a flow rate of 0.4 ml/min), with 10 ml increments sampling.

## Leaching results and discussion

Eight samples from three different geographical locations (Madagascar, Brazil and South-East Asia) were tested. The individual *REE* content of the original samples was measured by ICP-OES and is given in Table 1 (expressed as ppm); the chondrite-normalized distribution, based on chondrite data from Taylor and McClennan (1985), is shown in Fig. 1.

Despite T*REE* content being consistent with grades expected for the ion-adsorption ores, no specific pattern of preferential *REE* accumulation and distribution was observed, except that all ores seem to be rich in La, Y and Nd; although some similarities in terms of relative composition are observed within deposits originating from the same geographical areas (e.g. A1 through A5), there is no consistent trend. This is due to wide variations in composition of original host rocks and

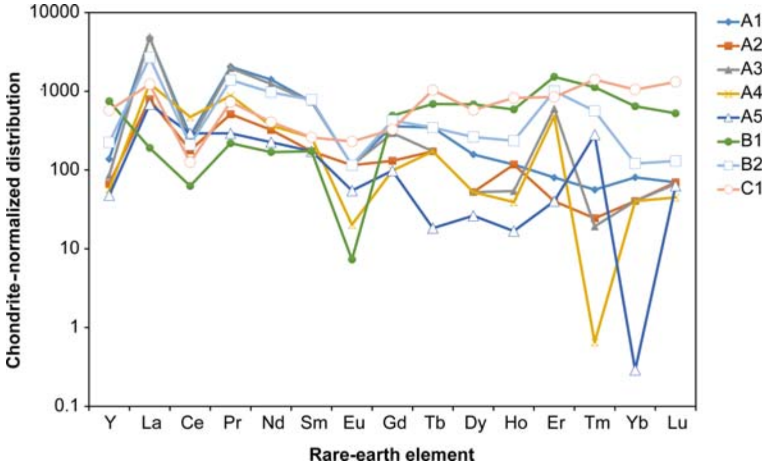


FIG. 1. Chondrite-normalized distribution of *REE* within ore samples.

incongruent dissolution-adsorption processes during the weathering processes, as shown by Bao and Zhao (2008), Sanematsu *et al.* (2013) and Xiao *et al.* (2015 *b*). Ores B1, B2 (South-East China) and C (Brazil) indicate higher content of *HREE* while A1 thorough A5 (Madagascar) seem to contain more *LREE*.

### *Batch leaching*

The ore samples listed in Table 1 were batch leached using the benchmarked procedure described above to investigate the terminal *REE* extraction levels (shown in Table 2) and T*REE* leaching kinetics, respectively (presented in Fig. 2).

From data in Table 2 it can be observed that all the minerals investigated are the ion-adsorption type, i.e. the lanthanides are physically adsorbed and can be easily recovered via a simple ion-exchange leaching procedure, as described by Moldoveanu and Papangelakis (2012, 2013). The extraction levels vary between 40 to 80%, consistent with the predicted exchangeable *REE* percentage, as described by Chi and Tian (2008). Again,

TABLE 2. Final *REE* extraction levels, expressed as %E (leaching + washing).

| Origin | Africa | | | | | Asia | | S. America |
|---|---|---|---|---|---|---|---|---|
| %E | A1 | A2 | A3 | A4 | A5 | B1 | B2 | C1 |
| Y | 77.3 | 72.6 | 93.6 | 67.1 | 57.2 | 80.5 | 79.9 | 70.8 |
| La | 83.6 | 76.9 | 92.7 | 66.4 | 61.2 | 85.0 | 80.5 | 82.9 |
| Ce | 0.0 | 16.9 | 12.6 | 6.8 | 11.6 | 0.0 | 0.0 | 35.6 |
| Pr | 75.1 | 65.0 | 92.3 | 74.1 | 35.1 | 62.9 | 69.4 | 72.8 |
| Nd | 80.8 | 74.1 | 90.3 | 68.0 | 46.0 | 86.3 | 87.9 | 83.2 |
| Sm | 90.6 | 85.2 | 97.1 | 66.3 | 96.4 | 43.1 | 81.2 | 76.9 |
| Eu | 62.1 | 79.0 | 89.1 | 43.8 | 84.3 | 61.3 | 83.0 | 36.2 |
| Gd | 82.6 | 63.0 | 82.8 | 74.8 | 62.3 | 90.1 | 84.9 | 61.6 |
| Tb | 84.1 | 62.8 | 74.6 | 19.2 | 37.3 | 91.5 | 90.1 | 35.6 |
| Dy | 80.9 | 76.3 | 97.4 | 74.2 | 52.2 | 87.5 | 79.7 | 61.5 |
| Ho | 75.5 | 0.0 | 96.1 | 96.9 | 97.5 | 82.9 | 77.2 | 51.8 |
| Er | 86.8 | 73.5 | 80.2 | 63.0 | 44.7 | 75.2 | 91.5 | 53.0 |
| Tm | 53.4 | 79.4 | 30.0 | 23.1 | 7.0 | 57.9 | 26.8 | 47.0 |
| Yb | 73.2 | 64.0 | 17.6 | 16.0 | 25.4 | 77.9 | 73.2 | 61.9 |
| Lu | 52.3 | 34.9 | 33.7 | 31.7 | 12.2 | 78.5 | 67.5 | 51.5 |
| T*REE* | 76.6 | 64.0 | 76.7 | 57.1 | 42.6 | 80.3 | 82.1 | 68.7 |

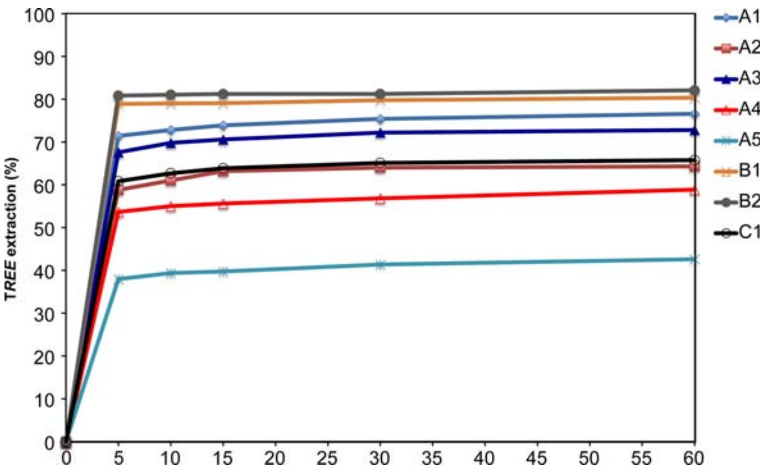


FIG. 2. Kinetic response of ion-adsorption ores from various geographical origins to benchmark leaching conditions (0.5 M $(NH_4)_2SO_4$, 30 min leaching, ambient conditions).

there is no consistent trend regarding *REE* desorption within clays of similar geographical origin; this could be explained in terms of: (1) The ores may contain a higher percentage of clays with lower cation exchange capacity (CEC) such as kaolinite, that will adsorb fewer ions than the ones with larger CEC such as smectites, hence less is available for desorption (possibly observed for A5). (2) The overall exchangeable fraction of *REE* is low, regardless of the high *REE* content; probably the majority of the total *REE* content is locked in the mineral matrix (possibly observed for clays A4 and C1).

As a general trend for all ion-adsorption ores, the percentage of extracted cerium is significantly lower than that of other *REE* due to its presence mostly as $CeO_2$ while some of the *HREE* also show poor extraction probably because of the stronger adsorption, as described by Coppin *et al*. (2002).

In terms of extraction kinetics, all materials investigated showed a common trend of fast *REE* desorption which is the typical behaviour of the ion-adsorption minerals. While each clay sample possesses a slightly different *REE* content and *REE* extraction end point, it can be seen that extractions reach the terminal levels in a very similar fashion, typically reaching a plateau in <15 min of batch leaching time. Moldoveanu and Papangelakis (2013) demonstrated that desorption kinetics are very fast and independent of temperature, pH, and agitation rate, but there is an effect on the terminal extraction levels.

### *Maximizing REE extraction*

As the leaching process can be considered an ion exchange process at equilibrium, the authors investigated whether all the extractable *REE* are indeed recovered during the initial leaching stage. One possible option to increase *REE* extraction from the clays is through multi-stage leaching using fresh lixiviant: i.e. the clays were leached, vacuum filtered, washed twice and re-leached with fresh solution for a total of three times, following the same base-line procedure; a L:S ratio of 2:1 was used for each leaching stage. The ore A4 was selected for this experiment as it showed somehow lower T*REE* %E (percent extractions) during the initial leaching step (Table 3) – thus raising the

TABLE 3. Performance comparison batch *vs*. column leaching (ore A4).

| Process | Mass of clay (g) | Mass of *REE* on clay (mg) | Mass of *REE* extracted (mg) | %E (T*REE*) |
|---|---|---|---|---|
| Column leaching | 223 | 310 | 163 | 53 |
| Column leaching + wash | 223 | 310 | 186 | 60 |
| Batch leaching + wash | 100 | 139 | 75 | 57 |

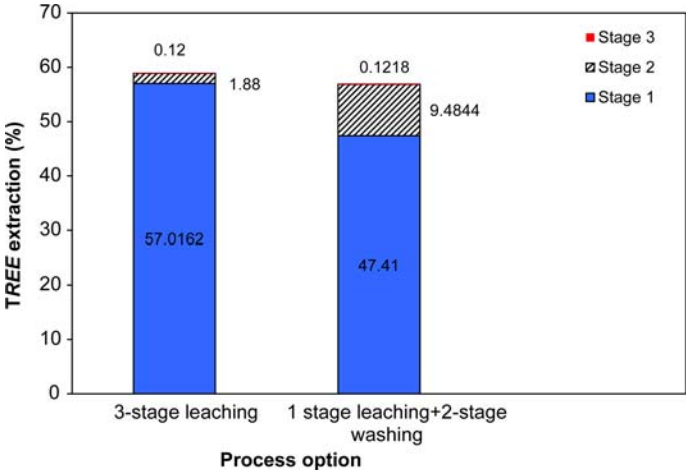


FIG. 3. Impact of multi-stage leaching and cake washing on overall T*REE* extraction (A4 ore, L:S = 2:1, 30 min leaching under ambient conditions).

possibility that more could be extracted via repeated leaching; the results are presented in Fig. 3.

It can be seen that multi-stage leaching of clays with fresh solution provided no benefit to additional extraction, increasing the overall T*REE* extraction by only ~1.88%; therefore, further use of fresh lixiviant is not recommended as it does not improve %E (this behaviour has been observed consistently for all ion-adsorption ores investigated). Proper washing of leached material, however, plays an important role in maximizing the recovery of *REE* and the unspent lixiviant. Figure 3 also shows the distribution of T*REE* recovery between the initial stage leachate, the first washing step and a second washing step for a single-stage leaching experiment. It can be observed that washing accounted for ~9.5% of the T*REE* recovered from leachate retained in the filter cake – and it is therefore an essential and strongly recommended step.

### *Leachate loading*

While maximum *REE* extraction is the primary objective of the leach process, it is important to note that the *REE* concentration of the resultant leachate impacts on the downstream circuit. High *REE*

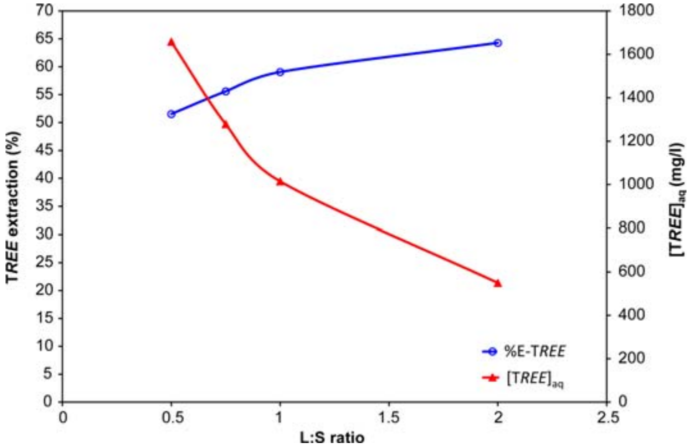


FIG. 4. Impact of L:S ratio on total *REE* extraction and leachate *REE* concentration (A2 ore, 30 min leaching under ambient conditions).

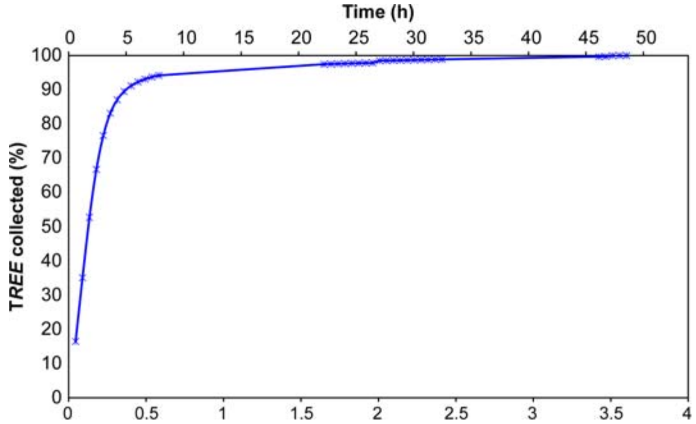


FIG. 5. Column leaching results as a function of L/S ratio and time (A4 ore, 0.4 ml/min flow, ambient temperature).

concentration reduces the circuit size of the downstream precipitation process.

The *REE* concentration in the leach solution increases with decreasing L:S ratio. As the total amount of ammonium in solution is usually well in excess of the stoichiometric requirement to desorb *REE*, decreasing the L:S ratio has a minor impact on maximum extraction. In this part of the study, the ore A2 was leached using the standard leaching procedure described in the experimental section, with L:S ratios of 0.5, 0.75, 1 and 2.

Figure 4 shows the total *REE* extractions expressed as %E, and the resultant total *REE* concentrations in the leachate expressed as $[TREE]_{aq}$. It can be seen that, while an extraction improvement by 10–20% units was observed when the L:S ratio was increased from 0.5 to 2, the T*REE* concentration in the leachate dropped due to dilution. Additionally, as the L:S ratio decreased, agitation became increasingly more difficult due to increased slurry viscosity; slurries with L:S ratios below 0.5 were virtually impossible to agitate. Hence, a L:S ratio of 1.5–2.0 was deemed to be the optimal.

Recent research studies by the authors (Cheuk *et al*., 2014) demonstrated that reusing loaded leachate on fresh ores (i.e. leachate recycling) and multi-stage counter-current leaching were all capable of increasing *REE* concentrations in the resultant leachate, though at the expense of *REE* extraction levels.

### *Column leaching studies*

An alternative technique of increasing leachate loading and decreasing L/S ratio is column

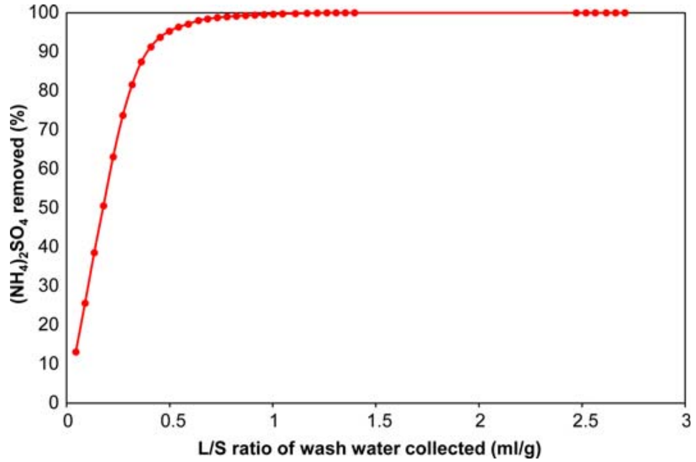


FIG. 6. Column residue washing (A4 ore, 0.4 ml/min flow, deionized $H_2O$ of pH 5, ambient temperature).

leaching, which simulates heap and/or *in situ* leaching processes presently practiced in the field (Chi *et al*., 2014). The column leaching tests were performed on the ore A4, according to the procedure described in the Experimental section.

The total *REE* extraction as a function of lixiviant volume collected over 48 h (expressed in volume per unit mass of ore) is shown in Fig. 5. It can be observed that ~94% of the total *extracted REE* (referenced to a terminal extraction of ~53%) is collected in the first ~0.6 ml/g of leachate (corresponding to 120 ml lixiviant) after 9 h of operation. It appears that increasing the column operation beyond 1.5 ml/g or 20 h would only bring minimal extraction improvement.

In order to completely elute all *REE* in the column and to ensure that the solid residue is free of lixiviant prior to disposal, column flushing with fresh water becomes necessary – and the results are shown in Fig. 6. It can be observed that ~99% of $NH_4^+$ was removed in the first 1.06 ml/g wash water collected (corresponding to ~234 ml of $H_2O$) after 13 h of operation.

For an overall comparison, Table 3 shows %E (T*REE*) for batch and column leaching modes, respectively. It can be observed that, for much lower L/S ratios (0.5–1.0), the column leach achieves T*REE* extraction levels similar to the batch process (which employs a L/S ratio of 2), and better extraction than batch when column flushing (washing) is performed.

## Conclusions

The leaching performance of ion-adsorption *REE* deposits outside China have been demonstrated and a unified benchmark procedure for *REE* leaching from these types of ores has been established. It was found that, regardless of variations in ore origin and *REE* content, all *REE* consistently reached peak extraction levels under ambient conditions with fast kinetics. However, the final overall extractions were generally element-specific, i.e. not all *REE* reached similar recovery levels for a given ore, as shown in Table 2.

Various techniques to improve the *REE* extraction through process variations were also investigated. It was found that decreasing the L:S ratio, leachate recycling and counter-current operation were all capable of increasing *REE* concentrations in the resultant leachate, however, at the expense of *REE* maximum extraction levels.

Column leaching provides a more efficient alternative to the batch process, achieving similar or better *REE* extraction levels with lower lixiviant use and constitutes an important step towards simulating the heap or *in situ* leaching. The water trapped in leached ore residues was found to contain significant amounts of *REE* and residual lixiviant necessitating significant washing for increasing *REE* recovery and environmental compliance.

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